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(54) **Oil field cementing methods and compositions.**

(57) Cementing compositions, and methods of using such compositions in oil, gas and water well cementing operations to reduce fluid loss from the composition to the formation, incorporate certain copolymers of N,N-dimethylacrylamide and 2-acrylamido-2-methyl propane sulfonic acid having mole ratios of between 1:4 and 4:1 respectively and average molecular weights of between about 75 000 and about 300 000.

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OIL FIELD CEMENTING METHODS AND COMPOSITIONS

This invention relates to cementing compositions and their use in oil wells and the like.

For oil field cementing operations to be successful, additives which reduce fluid loss are required to be added to the cement. Such additives will be used in well cementing operations where the bottom hole circulating temperatures (BHCT) may range from 80° - 170°F., substantial salt concentrations may be present, and slurry retardation and viscosity are critical aspects as same affect pumpability and compressive strength.

The present invention relates to an aqueous cementing composition and method of using same in cementing oil and gas wells and the like. More particularly the present invention concerns incorporation of copolymers of N,N-dimethylacrylamide and 2-acrylamido-2-methyl propane sulfonic acid in a hydraulic cement for the purpose of reducing fluid loss during cementing operations.

Certain polymer compositions have long been recognized by those skilled in the art of cementing wells in the petroleum industry as cementing additives useful in reducing fluid loss from a slurry of cement and water to the surrounding environment, i.e. the formation. These compositions are commonly referred to as "fluid loss additives."

An example of a fluid loss additive for use in an acidizing or fracturing composition is found in U.S. Patent No. 4,107,057. In the '057 patent a copolymer of a sulfonic-acid modified acrylamide and a polyvinyl cross-
5 linking agent is employed.

In the oil well cementing art, a variety of polymers have been disclosed as useful fluid loss additives for hydraulic oil well cements. For example, U.S. Patent No. 4,015,991 discloses such a fluid loss additive for a
10 hydraulic cement slurry consisting of hydrolyzed copolymers of acrylamide (AA) and 2-acrylamido, 2-methyl propane sulfonic acid (AMPS). However, these AA/AMPS copolymers are useful only in operations where the bottom hole circulating temperature (BHCT) ranges from 90°-125°F, whereas BHCT
15 ranges encountered in such operations are often outside such a range. Still further, these copolymers have a salt tolerance of only up to about 10%.

The temperature limitations of the AA/AMPS copolymers, i.e. loss of usefulness above about 125°F. BHCT, are
20 believed to be the result of hydrolysis of the amide groups. The carboxylate groups formed by such hydrolysis convert the copolymers to materials which function to retard the setting of the cement and to reduce the compressive strength of the set cement. Further, in the lower portion of the above mentioned temperature range (between 90°-100°F.) the AA/AMPS
25

copolymer is less effective as a fluid loss additive, requiring inclusion of larger amounts of such additive than at higher temperatures. The inclusion of sufficiently large amount of additive to create an acceptable fluid loss com-
5 position often creates viscosity and pumpability problems, since the addition of such copolymer directly affects the resultant slurry rheology. Copolymers of acrylamide and AMPS exhibit high viscosity and poor mixability, resulting in cement slurries having poor pumpability characteristics
10 during cementing operations. Mixability is a subjective term used to describe how well the components in the cement composition wet and mix with each other, as well as the energy required to create a generally homogeneous slurry.

Hence, the industry desires a fluid loss additive
15 that has as little effect on compressive strength, set time, viscosity, and thickening time as possible; is salt tolerable, i.e. does not exhibit substantial loss of effectiveness in the presence of salt; and is chemically stable during cementing operations. Further, such desired fluid
20 loss additive should be compatible with as many other additives and environmental conditions as possible, should be soluble in cement slurries at normal ambient temperature encountered in oil well cementing operations, as well as to continue to provide fluid loss characteristics over broad
25 temperature and cement pH ranges.

U.S. Patent No. 4,404,111 discloses the use of copolymers of N,N, dimethylacrylamide and 2-acrylamido, 2-methyl propane sulfonic acid as viscosity control agents in aqueous compositions to facilitate petroleum recovery from subterranean bearing formations. The method of preparing said copolymers uses conventional free radical initiators such as ammonium persulfate and results in copolymers having average molecular weights of greater than about one million. Further, the amount of NNDMA monomer employed in preparing the AMPS/NNDMA copolymer is disclosed as between 70 to about 99.5 weight percent.

SUMMARY OF THE INVENTION

Cementing compositions for use in oil, gas and water well cementing operations are disclosed. More particularly, such compositions are comprised of water, hydraulic cement and certain copolymers of N,N, dimethylacrylamide ("NNDMA") and 2-acrylamido, 2-methyl propane sulfonic acid ("AMPS"). Such copolymers are fluid loss additives having a NNDMA/AMPS monomer ratio of between 4:1 and 1:4 and average molecular weights such that a 1000 ppm aqueous solution of said copolymers has a Brookfield viscosity reading at 5 rpm of the U.L. Adapter Spindle in the range between about 30 and about 250 centipoise. The copolymers used in the present invention are relatively stable

to hydrolysis over a wide range of temperature and pH. Such copolymers may be admixed in solid form with any dry hydraulic oil field cement or may be added at the time the cement slurry is being prepared, either to the mixing water
5 or to the slurry. Additionally, methods of cementing a conduit in a borehole penetrating an earthen formation by introducing such a cementing composition into the space between such conduit and formation are disclosed.

So that the above-recited features, advantages and
10 objects of the invention, as well as others which will become apparent, are attained and can be understood in detail, more particular description of the invention is set forth below with respect to typical embodiments thereof, but the described embodiments should not be considered limiting
15 of its scope, for the invention may admit to other equally effective embodiments which will be apparent from the description to one of ordinary skill in the art.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

20 New cementing compositions and methods of using same in oil, gas and water well cementing operations are disclosed. Such compositions are comprised of water, hydraulic cement and a fluid loss reducing additive comprised of a copolymer NNDMA/AMPS wherein said copolymer
25 has a NNDMA/AMPS mole ratio of between 1:4 to 4:1, and a

molecular weight such that the Brookfield viscosity reading of a 1000 ppm aqueous solution of said copolymers at 5 rpm of the U.L. Adapter Spindle is in the range of between about 30 and about 250 centipoise. More preferably, the

5 Brookfield viscosity reading is between about 130 and about 200 centipoise. Further, where such cementing compositions contain salt in an amount up to about 18% by weight of water, then the preferred mole ratio of NNDMA to AMPS is about 1:1.5.

10 The cementing compositions of the present invention are useful in oil, gas and water well cementing operation since such compositions have reduced fluid loss to the surrounding formation. Such compositions are used to cement a conduit penetrating a permeable earthen formation via
15 introducing such composition into the space between such conduit and such formation and allowing the composition to harden.

The copolymers used in the present invention may be manufactured in accordance with various well known free-
20 radical techniques. However, in the present invention new solution polymerization techniques were employed to obtain polymer solutions of NNDMA and AMPS containing 10% by weight of solids. Such polymerization techniques are described in an application for patent filed on even date herewith by S.
25 Prabhakara Rao. The mole ratios of the NNDMA and AMPS mono-

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mers are variable, but for the purposes of this invention should not vary in ratio amounts greater than 4 to 1 in either direction.

A number of materials were tested as potential
5 fluid loss additives, including NNDMA/AMPS copolymers.
These tests were performed at 100°F. using Class H cement and 46% water by weight of dry cement. The additive containing cement slurries were mixed in a Halliburton Consistometer and stirred for twenty minutes. The
10 Halliburton Consistometer is a non-pressurized device that simulates a cement pumping process via movement of the consistometer can about a static paddle. Temperature can be varied but pressure is atmospheric. Fluid loss was measured at 1000 psi through a 325 mesh screen in cc/30 min. The
15 results of these fluid loss tests are provided in Table I.

The Table I test results indicate that certain copolymers of NNDMA/AMPS are effective fluid loss additives under static 100°F temperature conditions.

Table I
Fluid Loss Tests on Several Polymers
Base Slurry - Class H Cement + 46% Water - Temperature -100°F

Polymer Name (Mole Ratio)	Polymer By Weight of Dry Cement	Consistometer Reading		Fluid Loss in cc/30	
		0 min	20 min	min- 1000 psi and	a 325 mesh screen
Poly dimethylamino propylamino aspartamide	1.5	3	7		1860
Copolymer of AMPS and NNDMA (1:1)	0.2 0.4	4 9	7 9		94 28
Copolymer of acrylamide and NNDMA (1:1)	0.6	10	11		298
Copolymer of AMPS and NNDMA (1:4)	0.6	9	9		34
Copolymer of acrylamide and DMAEMA (2.8:1)	0.5	4	9		672
Copolymer of AMPS and cationic methacrylate (2:1)	0.6	3	9		347
Copolymer of AMPS and DMAEMA (1:2.6)	0.6	4	6		1491
Homopolymer of NNDMA	0.6	9	10		330
Homopolymer of DMAEMA	0.6	4	9		923
Copolymer of Vinylamine and AMPS (1:1)	0.6	3	7		1128
Copolymer of acrylamide and AMPS (4:1)	0.6	15	11		86

NNDMA: N, N, Dimethylacrylamide.

AMPS: 2-Acrylamido, 2-methyl propane sulfonic acid.

DMAEMA: Dimethylamino ethyl methacrylate.

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To determine whether copolymers of AMPS/NNDMA are sensitive to temperature variations, tests were conducted in the same manner as above at temperatures ranging 80°, 100°, 125° and 172°F. Additionally, various mole ratios of AMPS/NNDMA were evaluated. The results, as provided in Table II, indicate that such copolymers of AMPS/NNDMA are effective fluid loss agents over a broad range of temperatures. Additionally, this data indicates that there is limited fluid loss variation with variation of the mole ratio of AMPS/NNDMA when the amount of AMPS/NNDMA present remains constant at 0.6% by weight of dry cement.

Table II
Fluid Loss of Several AMPS - NMDA
Copolymers of Varying Monomer Ratio

% of AMPS/NMDA Copolymer by Wt. of Dry Cement	Mole Ratio AMPS/NMDA	Halliburton Consistometer Rheology at 0 Min./Rheology after 20 Min.					Fluid Loss - 1000 psi cc/30 min			
		80°F	100°F	125°F	172°F		80°F	100°F	125°F	172°F
0.60	1:1.5	19/16	13/12	15/11	12/10		22	26	26	32
0.60	1.5:1	7/8	6/8	5/6	5/6		34	40	44	58
0.60	2:1	10/13	9/10	8/10	—		22	24	28	—
0.60	3:1	7/11	7/9	6/8	5/7		24	26	28	44
0.60	3.5:1	7/10	6/9	6/8	5/7		24	26	30	44

Base Slurry: Class H Cement + 46% H₂O by weight of dry cement.
AMPS: 2-Acrylamido, 2-methyl propane sulfonic acid.
NMDA: N, N, Dimethylacrylamide.

Table III provides test results where the mole ratios of the AMPS/NNDMA copolymers were varied between 1:4 and 3.5:1. Further, the slurries containing these copolymers contained sea water or salt in an amount of 10%, 18% or sufficient to cause saturation. Although the data found in Table II indicate that variation in the mole ratio of AMPS/NNDMA present in fresh water slurries has little affect on fluid loss properties, results in salt water are much different. The data found in Table III indicates that the copolymers tested respond differently when salt concentrations are varied. As the salt concentration is increased, there is an increase in fluid loss. The copolymer additive was very effective when used in sea water slurries, with fluid loss variance measured between 26 and 46. In a 10% salt by weight of water slurry the fluid loss properties were excellent in the percent additive range of 0.8% or 1.0% by weight of dry cement, except for the 4:1 and 1:3.5 mole ratio of AMPS/NNDMA containing slurries. The slurries containing only 0.6% of additive by weight of dry cement were less effective. To maintain the degree of effectiveness, it is necessary to increase the amount of copolymer additive as the amount of salt is increased. This is further illustrated in the 18% by weight of water and saturated salt slurries. However, it should be noted that as the amount of copolymer additive is increased, the rheology of the slurry

also increases. From an operations standpoint, slurries having a rheology measured above about 12-15 Bearden units of consistency on the Halliburton Consistometer become less desirable and increasingly less desirable as that number increases.

Although the amount of copolymer present may be varied, a generally effective amount will be from about 0.1% to about 1.5% by weight of dry cement. Such an effective amount will depend on the amount of salt and water present, temperature, average molecular weight of the copolymer, rheological considerations and other additives present.

Table III

Fluid Loss and Viscosities of Various AMPS-NDMA Copolymers
In Salt and Sea Water Slurries at 125°F (Base slurry: Lone Star Class H Cement + 46% Water by Wt. of Dry Cement)

Mole Ratio AMPS/NDMA	% Additive by wt. of Dry Cement	Halliburton Consistometer Rheology at 0 Min./Rheology After 20 Min.				Fluid Loss - 1000 psi cc/30 min			
		10% Salt		18% Salt		Sea Water	10% Salt	18% Salt	Sat'd Salt
		by wt.	of H ₂ O	by wt.	of H ₂ O				
1:4	0.6	12/12	11/15	10/11	10/9	36	143*	153*	464*
1:1	0.6	19/10	9/10	9/10	10/14	40	76	138*	421*
1.5:1	0.6	15/10	9/11	8/10	9/15	34	50	132	474*
2:1	0.6	9/8	7/8	9/12	10/12**	38	52	163*	563*
3.5:1	0.6	5/7	6/7	6/8	8/11	46	360*	468*	700*
1:1	0.8	—	14/14	12/15	12/17	—	28	40	312*
1.5:1	0.8	—	10/14	10/14	8/13	—	38	90	335*
2:1	0.8	14/15	10/11	9/11	10/14**	26	32	120	332*
1:1	1.0	—	20/20	15/19	13/17	—	22	24	168*
1.5:1	1.0	—	13/14	13/15	10/16	—	30	40	208*
2:1	1.0	—	11/12	10/11	10/19	—	28	48	179*
3.5:1	1.0	—	8/10	—	—	—	344*	—	—
1:4 ***	0.6	30/12	14/10	15/10	23/10	156	64	70	287

* Calculated

** Slurry tended to gel at the top of the Halliburton Consistometer paddle

*** This additive was a copolymer of AMPS and acrylamide having a mole ratio of 1:4 AMPS/acrylamide

AMPS: 2-Acrylamido, 2-methyl propane sulfonic acid.

NDMA: N, N, Dimethylacrylamide.

When used in cement slurries containing appreciable amounts of salt, the most preferred fluid loss additive copolymer of 2-acrylamido, 2-methyl propane sulfonic acid (AMPS) and N,N, dimethylacrylamide (NNDMA) has a 1.5:1 AMPS/NNDMA mole ratio. Good fluid loss properties are exhibited when the mole ratio of NNDMA:AMPS is varied from about 4:1 to about 1:4. However, as the AMPS:NNDMA mole ratio is varied away from the about 1.5:1 most preferred range, the fluid loss characteristics in such salt-containing slurries are diminished. Such copolymers can be prepared with a variety of molecular weights.

Table IV

Brookfield Viscosity Measurements of AMPS - NNDWA (1.5:1 mole ratio)
Copolymers of Varied Molecular Weights

Sample	Percent of Polymer in Solution	Brookfield Viscosity* of a 1000 ppm polymer solution at			Viscosity in Centipoise of a 1000 ppm polymer solution at		
		1 rpm	2.5 rpm	5 rpm	1 rpm	2.5 rpm	5 rpm
(1)	10	18	41	77.5	288	262	248
(2)	10	14	30.5	58.5	224	195	187
(3)	10	12	24	48.5	192	153	155
(4)	10	10.5	24.5	48	168	156	153
(5)	10	9.5	21	42	152	134	134
(6)	10	3.5	7.5	15.5	56	48	49
(7)	10	2	4.5	9	32	29	29
(8)	10	2	4	8	32	25	25

AMPS: 2-Acrylamido, 2-methyl propane sulfonic acid.

NNDWA: N, N, Dimethylacrylamide.

* Measured on RVT instrument with U.L. Adapter.

Eight copolymers having a molar ratio of 1.5:1 AMPS/NNDMA were synthesized. The absolute molecular weights of these polymers were not determined. However, the samples were graded in decreasing order of molecular weight by viscosity using a 1000 parts per million concentration of copolymer in water. The viscosities were measured on a Brookfield viscometer with "New UL Adapter" using "RVT factors" supplied by the manufacturer. Spindle speeds of 1, 2.5 and 5 RPM were used. The values obtained at 5 RPM were used for comparison of viscosities. The polymer solutions were prepared by diluting the stock solutions of the polymers obtained from the polymerization equipment to 1000 ppm. The solid contents of the stock solutions were previously estimated by precipitation of the polymers by acetone and weighing the dried polymer. The viscosities were expressed in centipoise at a given RPM of the spindle. This data is provided in Table IV.

The molecular weight of the copolymer is important for rheological reasons. As the molecular weight of the copolymer is increased, the viscosity of the cement slurry increases, finally reaching a point where it is essentially no longer pumpable. This point is reached when the Brookfield viscosity reading of a 1000 ppm solution of copolymer at 5 rpm of the U.L. Adapter Spindle is somewhere above a reading of 250 centipoise. Such reading corresponds

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approximately to a molecular weight of about 300,000. On the other hand, when under the same conditions, this Brookfield viscosity reading drops below a value of about 30 (which corresponds to a molecular weight of about 75,000), such copolymer's fluid loss characteristics diminish below an essentially effective level.

Although the proportionality between the solution viscosity and molecular weight of a macromolecule is an established fact, deviations occur with variation in copolymer composition, sequence length of the units, intermolecular and intramolecular interaction between the side chains and the overall conformation of the molecule. Rather simple and accurate results may be obtained when predicting the solution viscosity of a homopolymer of a given molecular weight if a calibration is available, however, the same prediction is more arbitrary in the case of copolymers such as the NNDMA/AMPS copolymers of the present invention which contain strongly ionizing $-\text{SO}_3\text{H}$ units as well as $-\text{N}(\text{CH}_3)_2$ groups which can be protonated under strongly acidic conditions. In other words, two samples of the copolymers of the same composition and molecular weight may have widely differing solution viscosities depending on sequence length of the component monomer units, which length is governed by the reaction conditions employed during polymerization.

The Samples (1), (2), (4), (5), (6) and (8) of Table IV were tested for fluid loss properties. Samples

(1), (2), (4), (5) and (6) performed similarly in fresh water. Sample (8) did not provide good fluid loss properties in fresh water. Thus, the molecular weight ranges of the copolymers should be between about 75,000 and about
5 300,000.

Tests relating to WOC (waiting time which is defined as the time required for the slurry to obtain a compressive strength of 500 psi) on cement and 24 hour compressive strengths were made with cement compositions
10 containing copolymers of NNDMA/AMPS having mole ratios of 1:1.5 and copolymers of AA/AMPS having mole ratios of 4:1 are provided in Table V. These tests indicate that cement slurries containing NNDMA/AMPS copolymers provide better compressive strengths and shorter WOC times than cement
15 slurries containing the AA/AMPS copolymers.

Table V
Effects of Fluid Loss Additives on
Strength Development
Base Slurry - Class H Cement + 46% Water

Additive	Mole Ratio	% Additive By Weight of Dry Cement	Temp (°F)	Initial Set Time (hr:min)	WOC Time (hr:min)	24 Hour Compressive Strength (psi)
NNDMA/AMPS	1:1.5	0.6%	80	9:25	14:57	940
NNDMA/AMPS	1:1.5	0.8%	80	8:57	14:26	980
AA/AMPS	4:1	0.8%	80	12:32	22:40	590
NNDMA/AMPS	1:1.5	0.6%	100	7:01	10:12	1410
NNDMA/AMPS	1:1.5	0.8%	100	6:49	10:30	1390
AA/AMPS	4:1	0.8%	100	7:00	12:06	1270
NNDMA/AMPS	1:1.5	0.6%	120	3:58	6:10	2300
NNDMA/AMPS	1:1.5	0.8%	120	4:24	7:06	2000
AA/AMPS	4:1	0.8%	120	5:48	8:38	1760
NNDMA/AMPS	1:1.5	0.6%	140	3:11	5:07	2550
NNDMA/AMPS	1:1.5	0.8%	140	3:40	6:10	2080
AA/AMPS	4:1	0.8%	140	6:36	9:58	1420

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Hence, a preferred fluid loss additive copolymeric compound of NNDMA and AMPS has a mole ratio of about 1:4 to about 4:1 and a molecular weight of between 75,000 to about 300,000. When used in cement slurries containing appreciable amounts of salt, the most preferred fluid loss additive copolymeric compound of NNDMA and AMPS has a mole ratio of about 1:1.5 respectively and a molecular weight between 150,000 and 250,000.

CLAIMS:

1. A cementing composition for use in oil, gas and water well cementing operations comprising water, hydraulic cement, and a copolymer of N,N-dimethylacrylamide and 2-acrylamido-2-methyl propane sulfonic acid wherein said
5 copolymer comprises a ratio of N,N-dimethylacrylamide to 2-acrylamido-2-methyl propane sulfonic acid of from about 1:4 to about 4:1, and a molecular weight such that a 1000 ppm aqueous solution of said copolymer has a Brookfield viscosity reading at 5 rpm of the U.L. Adapter Spindle in
10 the range of between about 30 and about 250 centipoise.
2. A composition according to claim 1, wherein said copolymer is present in an amount of from about 0.1% to about 1.5% by weight of cement.
- 15 3. A composition according to claim 1 or 2, wherein said water contains up to about 18% salt by weight of water.
4. A composition according to claim 1,2 or 3, wherein
20 the mole ratio of N,N-dimethylacrylamide to 2-acrylamido-2-methyl propane sulfonic acid in said copolymer is 1:1.5.
5. A method of cementing a conduit in a borehole penetrating a earthen formation by introducing a cementing
25 composition into the space between said conduit and said formation, wherein said cementing composition is as defined in any of claims 1 to 4.
6. A method according to claim 5, wherein the
30 Brookfield viscosity reading of said copolymer is in the range of about 130 and 200.

7. A method according to claim 5 or 6, wherein said water contains up to about 18% salt by weight of water.

5 8. A method of cementing a conduit penetrating a permeable earthen formation by introducing a cementing composition into the space between said conduit and said formation and allowing said composition to harden, wherein the improvement comprises the use of a cementing composition
10 comprising water, wherein said water contains salt in an amount of up to about 18% by weight of said water; cement; and from about 0.1% to about 1.5% by weight of cement of a copolymer of N,N-dimethylacrylamide and 2-acrylamido-2-methyl propane sulfonic acid, having a mole ratio from
15 about 1:4 to about 4:1 and a molecular weight from about 150,000 to about 250,000.

9. A method according to claim 8, wherein the mole ratio of N,N-dimethylacrylamide to 2-acrylamido-2-methyl
20 propane sulfonic acid in said copolymeric compound is about 1:1.5.

